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SURFACE ENRICHMENT IN POLYMER BLENDS - A NEUTRON REFLECTION TEST*

by

R. J. Composto and R. S. Stein
Polymer Science and Engineering
University of Massachusetts
Amherst, MA 01003

E. J. Kramer and R. A. L. Jones
Dept. of Materials Science & Engineering
Cornell University
Ithaca, NY 14853

A. Mansour, A. Karim, G. P. Felcher
Materials Science Division
Argonne National Laboratory
Argonne, IL 60439

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ABSTRACT

In polymer melts of protonated and deuterated polystyrene (PS and d-PS) surface segregation of the d-PS occurs at temperatures and compositions in the one phase region close to the coexistence curve for phase separation. A neutron reflection test on a polymer blend containing 10% volume fraction of d-PS has shown that a thermal treatment caused a surface enrichment of d-PS up to 28%. The experiment demonstrates that neutron reflection measurements can generate detailed information on surface enrichment phenomena in polymer blends.

KEYWORDS

Neutron reflection, polymers, segregation

In compatible polymer blends, the phenomenon of surface enrichment (the equilibrium segregation of one component preferentially to the surface) is expected to be both ubiquitous and important practically in controlling properties such as the weatherability of the surface and its contact angle with various fluids. The expectation that surface enrichment is the rule rather than the exception in blends of high polymers stems from their very small combinatorial entropy of mixing which means that the concentration profiles associated with the segregation cost relatively little free energy if compared to small molecule systems. For large molecules the cost in the free energy of mixing can thus be less than the decrease in surface energy produced by replacing one component by the other at the surface; this cost can be further reduced near phase separation.

For very high molecular weight blends of PS and d-PS there is phase separation below a critical temperature[1]; below this temperature, the composition of the two phases in equilibrium is given by the coexistence (binodal) curve. Since the surface energy of d-PS is slightly less than that of PS, the surface of the blend should become enriched in d-PS upon annealing not too far above the coexistence curve. In this case the volume fraction of d-PS $\phi(z)$ versus z is thought to have the simple form[2]:

$$\phi(z)-\phi_\infty = (\phi_1-\phi_\infty)\exp(-z/\xi) \qquad (1)$$

where ϕ_∞ and ϕ_1 are respectively the bulk and surface volume fraction, and ξ is the correlation length. ϕ_1 and ξ have certain

analytical dependence[2] on the bulk composition of the blend as well as on the temperature of annealing.

Surface segregation in the d-PS:PS system has already been observed[3] by forward recoil spectrometry (FRES). Although this technique has a resolution of several hundred Ångstroms (a value considerably larger than a typical correlation length), it discriminates quite well light hydrogen from deuterium, so that the depth scan shows a peak of deuterium concentration at the sample surface. The integral of this peak is the "surface excess" z^*, which for the $\phi(z)$ profile of eq.(1) is given by: $z^*=(\phi_1-\phi_\infty)\xi$.

For a more complete mapping of the wetting phase diagram, it is desirable to measure separately ϕ_1 and ξ and to check if the analytical dependence of the volume fraction profile has indeed the form given[2] in eq.(1). In order to achieve this goal we have been experimenting with neutron reflection (NR), whose ultimate depth resolution is in the range of 10 Å. The technique, described in detail elsewhere[4], consists in sending a neutron beam of wavelength λ at grazing incidence θ to the sample's surface, and measuring the Fresnel reflectivity R as a function of the neutron momentum transfer $q_z=4\pi\sin\theta/\lambda$. The profile is an optical transform of the reflectivity[4]:

$$R(q_z) \longleftrightarrow b(z)/V(z) \qquad (2)$$

where b is the average nuclear scattering amplitude per unit volume V at the depth z from the surface. b/V for PS is 1.4×10^{-6} Å^{-2} while the corresponding value for d-PS is 6.5×10^{-6} Å^{-2}; while both quantities are small their contrast is excellent[5].

We report here on measurements of surface segregation made on a test sample, consisting in an homogeneous film of polystyrene of approximate thickness of 3000 Å. The volume fraction of d-PS in the blend was 10%. The film was spun cast from a toluene solution of 2wt% polymer directly on a round of fused silica, 5 cm in diameter and 1.3 cm thick (such thickness was required in order to keep the surface flat during the neutron experiment). The surface of the substrate had been polished to a finish of interferometer quality, with a flatness of 1/20 the wavelength of light; its unitary scattering amplitude for neutron was[6] $b/V = 3.48 \times 10^{-6}$ Å^{-2}. Both NR and FRES measurements were taken before and after annealing the sample at a nominal temperature of 184 C for 24 hrs in inert atmosphere. Because of the poor thermal conductivity of the silica substrate, the readings of the annealing temperature cannot be considered accurate: therefore for the present it is more meaningful to check the internal consistency of the measured data. The surface excess found for our annealed sample by FRES was $z^* = 22 \pm 5$ Å.

The neutron reflectivity measurements were performed at the reflectometer POSY at the Intense Pulsed Neutron Source of Argonne[4]. Fig.1 presents the experimental values of Rq_z^4 for the sample before and after annealing as a function of q_z. The reason for such a presentation is the following. Let us consider a uniform, infinitely thick polymer layer whose b/V at the surface is perturbed by ε over a thickness d. Neglecting higher order terms, at large q_z the average reflectivity is such that[7]:

$$(\pi/4)^2 q_z^4 R \simeq (b/V)^2 + 2(b/V)\varepsilon \qquad (3)$$

In other words, the function Rq_z^4 tends, for large q_z, to a constant which is characteristic of the system. Moreover the difference between the unperturbed and the perturbed reflectivities depends, in this limit, solely on the amplitude of the perturbation, and not on its thickness. For "large q_z" it is practically sufficient to start from a value three times that for total reflection. The considerations given above hold true even if the perturbing layer has an exponential decay, or if the polymer layer is relative thin and on a substrate; in the latter case, however, additional constants have to be added in eq.(3).

The experimental results are compared in Fig.1 with the reflectivities calculated for a model density profile air/polymer/glass. The reflectivities oscillate as a result of the interference between the reflection from the outer surface and from the polymer/glass interface, with a period due to a polymer thickness of 3250 Å. The pattern is progressively smeared by the finite resolution of the instrument (±0.015°). The density of the polymer film in the as-prepared-sample is taken as uniform, with a 10% volume fraction of d-PS. For the annealed sample we have to take into account a surface enrichment of d-PS. However, the range of q_z spanned by the experimental data is not sufficiently large to obtain an extrapolated value, and in the intermediate region the fittings of $\phi_1-\phi_\infty$ and ξ are not entirely independent. For instance the reflectivity calculated in Fig.1 is for a model where the enrichment of d-PS at the surface is $\phi_1-\phi_\infty=0.18$ with a correlation

length ξ= 70 Å; but a comparable fit to the data is obtained for $\phi_1-\phi_\infty$=0.14 and ξ=200 Å. These cases correspond to surface excesses z^*=13 and z^*=28 Å respectively, well encompassing the value determined by FRES.

In conclusio , both the forward recoil spectrometry and the present neutron reflection test are able to detect surface segregation even for a sample with a quite small surface excess. In a sense the two techniques are complementary: FRES establishes that there is a perturbation in concentration close to the outer surface, and then NR explores its shape; FRES determines the surface excess, $(\phi_1-\phi_\infty)\xi$, and NR is capable of separating the two quantities. This separation can be facilitated by expanding the region of q_z to to cover values for which eq. (3) is valid. The polymer samples should also have a substrate only weakly reflecting, not to overshadow the reflection from the surface excess. To illustrate these claims, we show in Fig. 2 the reflectivity calculated for the same polymer layer of Fig.1, but deposited on a silicon substrate ($b/V=2.08\times10^{-6}$ Å^{-2}). The continuous line is for $\phi_1-\phi_\infty$=0.18 and ξ=200 Å; the dashed line is for the same concentration at the surface but ξ=70 Å. The difference of the reflectivities for the two cases is now fairly dramatic, and shows how neutron reflection can best be exploited to determine the details of surface enrichment in polymer blends.

ACKNOWLEDGMENTS

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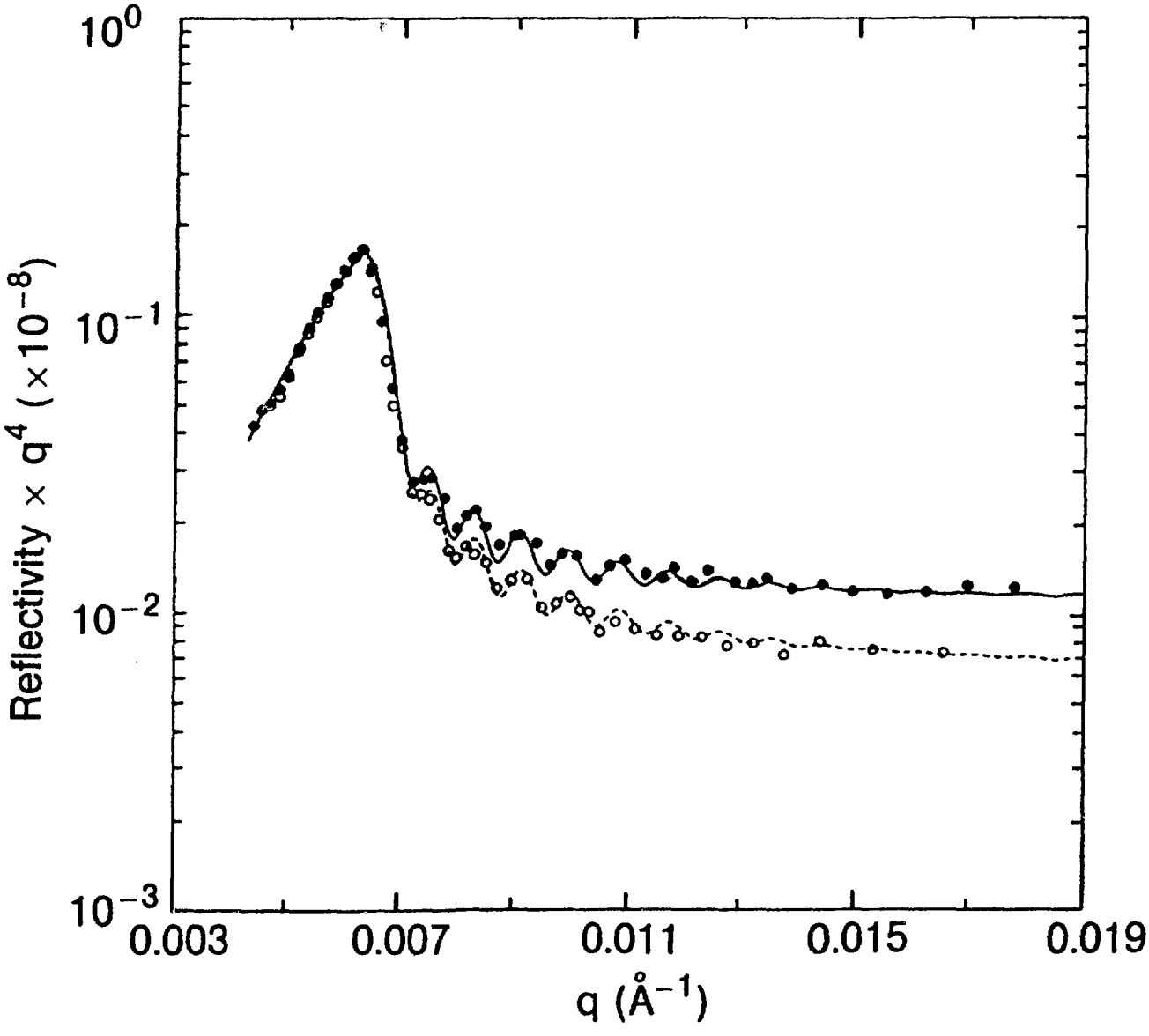
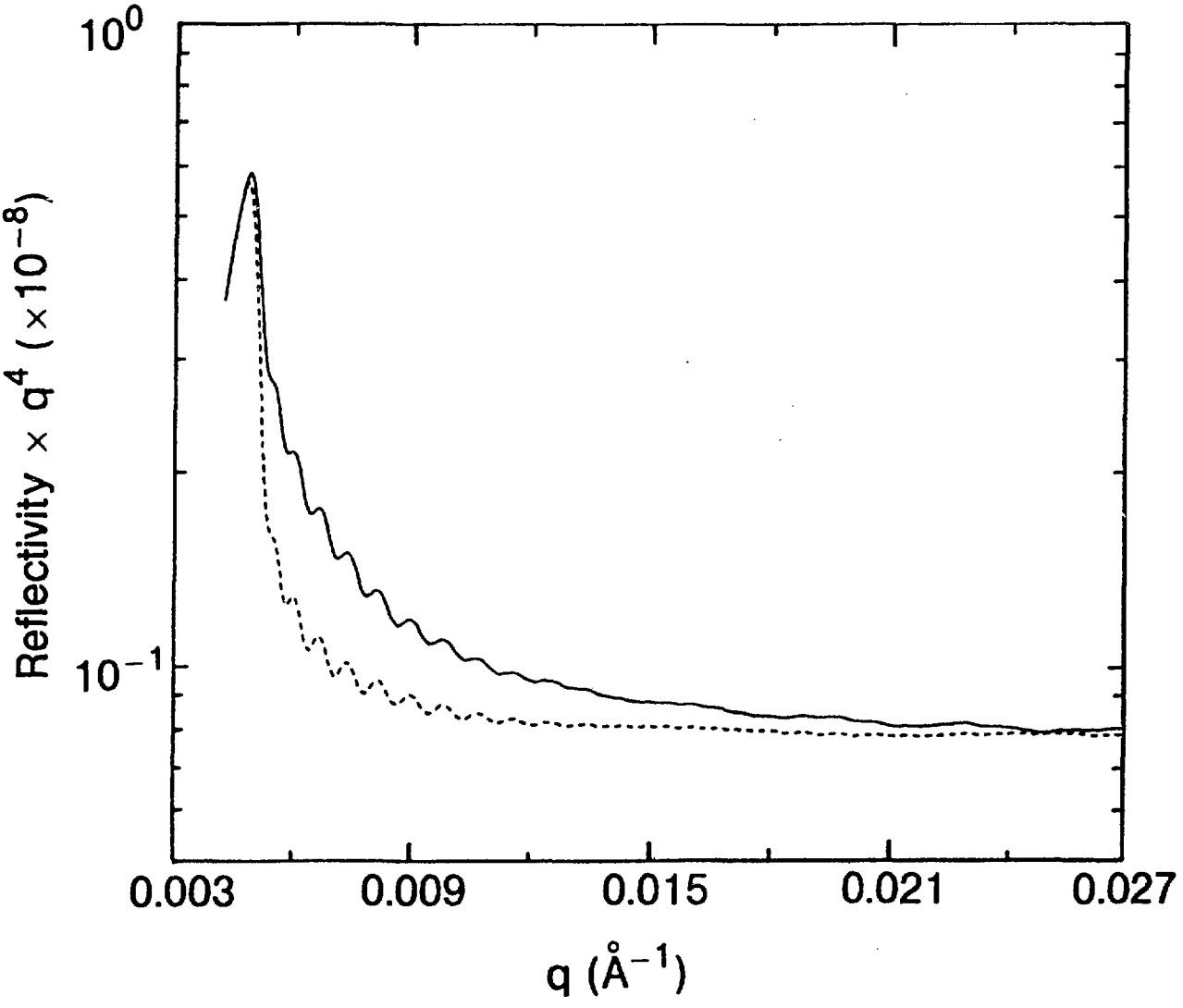
FIGURE CAPTIONS

Fig.1 Rq_z^4 for a polymer blend before (open circles) and after (full circles) annealing. The experimental data have been fitted with the model profiles (dashed and continuous lines) described in the text.

Fig.2 Rq_z^4 calculated for a film of d-PS:PS blend with a bulk volume fraction ϕ_∞=0.10 in d-PS. The film is 3250 Å thick on a silicon substrate. Dashed line is the film with surface volume fraction ϕ_1=0.28 with a correlation length ξ=70 Å. Continuous line: same surface enrichment, but ξ=200 Å.


10^0
10^{-1}
10^{-2}
10^{-3}
Reflectivity × q^4 (×10^{-8})
0.003
0.007
0.011
0.015
0.019
q (Å^{-1})


10^0
10^{-1}
Reflectivity × q^4 ($\times 10^{-8}$)
0.003
0.009
0.015
0.021
0.027
q ($Å^{-1}$)